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(54) **Fluid composition for compression refrigeration.**

(57) This invention provides fluid compositions for use in compression refrigeration comprising mixtures of
(a) at least one fluorohydrocarbon and
(b) at least one carboxylic ester of a polyhydroxy compound, having the general formula

$C(CH_2.O.CO.R)_n(R')_{4-n}$ (I)

wherein n is 3 or 4, R' represents a methyl or ethyl group and each R independently represents a C_{3-8} alkyl group containing 3 to 5 chain atoms.

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This invention relates to fluid compositions for use in compression refrigeration, more particularly to such compositions containing fluorohydrocarbon refrigerant, to the preparation of such compositions and to their use as refrigeration fluid in compression refrigeration equipment.

Fluid compositions for use in compression refrigeration comprise mixtures of at least one refrigerant and at least one lubricant. Compression refrigeration equipment includes refrigerators and air-conditioners, including automobile, domestic and industrial air-conditioning systems. Problems of lubrication are particularly evident in automobile air-conditioning systems, because such systems are not separately lubricated, and a mixture of refrigerant and lubricant circulates through the entire system. It is therefore important that the refrigerant and the lubricant should be compatible (naturally soluble) over wide ranges of temperatures and concentrations.

In the past, chlorofluorocarbons e.g. R-11 (CFC-11 R-12 (CFC-12) and R-113 (CFC-113) have generally been used as refrigerants.

JP-A-55-155093 discloses the use of chlorofluorcarbon refrigerants, specifically R-12 (HCFC-12) (dichlorodifluoromethane) and R-22 (chlorodifluoromethane), in combination with, as lubricant, neopentyl polyol esters containing 0.005 to 5% w of trimethyl phosphate. The neopentyl polyol is preferably trimethylolpropane or pentaerythritol, esterfied with straight-chain or branched saturated fatty acid esters, e.g. straight chain saturated fatty acids with 6 to 18 carbons such as caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, lauric acid, myristic acid, palmitic acid, or stearic acid, and synthetic branched saturated fatty acids with 8 to 18 carbons such as isocaprylic acid, 2-ethylhexoic acid, isononoic acid, isocapric acid, isolauric acid, isomyristic acid, isopalmitic acid or isostearic acid. 2-ethylhexoic acid is particularly preferred.

JP-A-61-171799 discloses the use of fluorocarbon refrigerants, the only named example of which is R-22 (HCFC-22) (chorodifluoromethane), in combination with, as lubricant, an ester-type oil together with, e.g. 0.02 to 10% w of, a hydroxy aryl fatty acid. The ester-type oil is preferably an ester of a monohydric alcohol and a dicarboxylic acid, an ester of a polyhydric alcohol, e.g. a neopentyl polyol, and a monocarboxylic acid, or as ester of a polyhydric alcohol and a mixture of monocarboxylic and dicarboxyl acids.

Owing to the ozone-depletion potential of most common chlorofluorocarbons (CFC's), global controls on their manufacture and application have been agreed under the Montreal Protocol (September 1987). Hydrofluorocarbons (HFC's) have been identified as potential alternatives to CFC's. Examples of HFC's include R-23 (HFC-23)(trifluoromethane), R-134 (HFC-134) (1,1,2,2-tetrafluoroethane), R-134a (HFC-134a) (1,1,1,2-tetrafluoroethane), R-143a (HFC-143a) (1,1,1-trifluoroethane) and R-152a (HFC-152a) (1,1-difluoroethane).

R-12 (CFC-12) (dichlorodifluoromethane) has been widely used in automobile air-conditioning systems and other compression-refrigeration equipment. R-134a (HF-134a)(1,1,1,2-tetrafluoroethane) has similar vapour pressure to R-12 and can in principle be used to replace R-12 without major redesign of existing compression -refrigeration equipment.

The problem that arises in relation to substitution of R-134a in place of R-12 is compatibility with lubricants. R-12 is compatible with mineral lubricating oils, whereas R-134a is not.

Polyalkylene glycols have been proposed as lubricants, e.g. Research Disclosure 17483, October 1978, by Du Pont and US Patent No. 4,755,316. However, of polyalkylene glycols it has been reported (Financial Times Wednesday November 28 1990, p14) ("FT article") that they "lubricated well but absorbed water and after a while began to react with other materials" in the compressors.

This same FT article states that "attention then switched to synthetic oils called polyol esters. Extensive testing of refrigeration equipment with these ester lubricants over the last few months has convinced the industry that they are the answer to its prayers. A combination of R-134a coolant with ester lubricant appears to work as well as R-12 plus mineral oil in domestic fridges, car air conditioners and small commercial refrigeration systems"

US Patent No. 4,851,144 proposes as lubricant compositions miscible with hydrofluorocarbon and hydrochlorofluorocarbon refrigerants, blends of polyether polyols with esters selected from esters of polyhydric alcohols with alkanoic acids and esters of alkanedioic acids with alkanols. In comparative test over temperature range -20°C to 85°C to determine upper solution critical temperature (USCT) using R-134a and various potential lubricants it was found (Table 1, Column 4) that a pentaerythritol tetraester of a mixture of alkanoic acids having 7-9 carbon atoms, 25% in R-134a, had USCT 80°C and trimethylol propane triheptonate, 16% w in R-134a, had USCT >83°C. WO 90/12849 discloses liquid compositions useful as refrigeration liquids in refrigerators and air-conditioners, comprising a major amount of at least one fluorine containing hydrocarbon containing one or two carbon atoms, most preferably R-134a, and a minor amount of at least one soluble organic lubricant comprising at least one carboxylic ester of a polyhydroxy

compound containing at least 2 hydroxy groups and characterised by the general formula

$R[OC(O)R^1]_n$

wherein R is a hydrocarbyl group, each R^1 is independently hydrogen, a straight chain lower (i.e. up to 7 carbon atoms) hydrocarbyl group, a branched chain hydrocarbyl group, or a straight chain hydrocarbyl group containing from 8 to about 22 carbon atoms provided that at least one R^1 group is hydrogen, a lower (i.e. up to 7 carbon atoms) straight chain hydrocarbyl or a branched chain hydrocarbyl group, or a carboxylic acid or carboxylic acid ester-containing hydrocarbyl group, and n is at least 2.

Specific examples of polyhydroxy compounds listed as useful in WO 90/12849 include ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, glycerol, neopentyl glycol, 1,2-, 1,3- and 1,4-butanediols, pentaerythritol, dipentaerythritol, tripentaerythritol, triglycerol, trimethylolpropane, sorbitol, hexaglycerol, and 2,2,4-trimethyl-1,3-pentanediol.

Examples of carboxylic acids containing a straight chain lower hydrocarbyl group include formic acid, acetic acid, propionic acid, butyric acid, pentanoic acid, hexanoic acid and heptanoic acid. Examples of carboxylic acids wherein the hydrocarbyl group is a branched chain hydrocarbyl group include 2-ethyl-n-butyric acid, 2-hexyldecanoic acid, isostearic acid, 2-methylhexanoic acid, 3,5,5-trimethylhexanoic acid, 2-ethylhexanoic acid, neoheptanoic acid, neodecanoic acid, and commercial mixtures of branched chain carboxylic acids such as the mixture identified as "Neo 1214" acid (trade mark) from Exxon. Examples of higher molecular weight (8 to about 22 carbon atoms) straight chain acids include decanoic acid, dodecanoic acid, stearic acid, lauric acid, and behenic acid.

Of the specific Examples in WO 90/12849, Example 6 describes reaction of trimethylopropane with a commercial C_{8-10} straight chain methyl ester followed by reaction with acetic anhydride. Example 9 describes (in the present tense) reaction of pentaerythritol with neoheptanoic acid followed by reaction with acetic anhydride to esterify remaining hydroxyl groups.

WO 90/12849 describes tests in which 0.5 g of various candidate lubricants (ester) and 4.5g R-134a (i.e. mixtures containing 10% w ester) are mixed and, if the lubricant is soluble in the R-134a, temperature is reduced until separation and/or precipitation occurs. For Example 6 this temperature is -45 °C. The lowest value obtained is -50 °C. No value is given for Example 9.

There has now surprisingly been found a defined class of polyol esters having significantly improved miscibility with R-134a, with respect to maximum and minimum miscibility temperatures, than any values hitherto reported.

According to the present invention there is provided a fluid composition for use in compression refrigeration comprising a mixture of

(a) at least one fluorohydrocarbon and

(b) at least one carboxylic ester of a polyhydroxy compound, having the general formula

$C(CH_2.O.CO.R)_n(R')_{4-n}$ (I)

wherein n is 3 or 4, R' represents a methyl or ethyl group and each R independently represents a C_{3-8} alkyl group containing 3 to 5 chain atoms.

The fluorohydrocarbon may be, for example trifluoromethane, 1,1,2,2-tetrafluoroethane, 1,1,1,2-tetrafluoroethane, 1,1,1-trifluoroethane or 1,1-difluoroethane, or a mixture of any two or more thereof but is preferably a tetrafluoroethane, more preferably 1,1,1,2-tetrafluoroethane (R-134a).

Fluid compositions of the invention may generally comprise, for example, 50 to 99% w of the at least one fluorohydrocarbon. Preferably the composition comprises a mixture containing 70 to 99% w, e.g. 80 to 98% w, of the at least one fluorohydrocarbon and 1 to 30% w, e.g. 2 to 20% w, of the at least one carboxylic ester.

Where n in formula I is 3, the esters are esters of trimethylolethane or, preferably, trimethylolpropane. Most preferably in is 4, in which case the esters are esters of pentaerythritol.

Each R in formula I independently represents a C_{3-8} alkyl group containing 3 to 5 chain atoms, By 3 to 5 chain atoms is meant that, starting with the carbon atom in R immediately adjacent the $CH_2.O.CO.$ moiety, the longest linear chain of carbon atoms in the R moiety contains 3 to 5 carbon atoms. Thus, for example, a R moiety of formula $-C(CH_3)_2CH_2CH_2CH_3$ is a C_6 alkyl group containing 4 chain atoms, and a R moiety of formula $-C(CH_3)(C_2H_5)_2$ is a C_6 alkyl group containing 3 chain atoms. Preferably each R independently represents a C_{4-6} alkyl group containing 3 to 4 chain atoms.

In accordance with a particularly preferred aspect of the invention there is provided a fluid composition for use in compression refrigeration comprising a mixture of at least one fluorohydrocarbon and at least one

carboxylic ester of a polyhydroxy compound, wherein the at least one carboxylic ester of a polyhydroxy compound consists of at least one ester having the general formula

$C(CH_2.O.CO.R)_4$ (II)

wherein n is 3 or 4, and each R independently represents a C_{3-8} alkyl group containing 3 to 5 chain atoms, more preferably a C_{4-5} alkyl group containing 3 or 4 chain atoms. It will be appreciated that formula II corresponds to formula I wherein n is 4.

Although each R moiety may be a C_{3-5} n-alkyl group (straight-chain alkyl group), in such cases the esters of formula I and II tend to have viscosity at 40°C (DIN 51 562) less than 20 mm^2/s.

Preferably the ester of formula I or II is an ester having viscosity at 40°C (DIN 51 562) of at least 20 mm^2/s wherein on average at least one R moiety is a branched alkyl group.

Fluid compositions in accordance with this invention may additionally include small quantities, e.g. 0.2 to 5%w, preferably 0.4 to 2.5%w, based on the weight of the at least one carboxylic ester, of each of one or more additives, such as thermal stabilisers (e.g. glycidyl ethers, for example phenyglycidyl ether), antiwear agents (e.g. steel/steel antiwear agents, for example "SANCTICIZER 154" (trade mark) ex Monsanto, and/or steel/aluminium antiwear agents, for example "VANLUBE 672" (trade mark) ex Vanderbilt) and metal passivators (e.g. copper passivators, for example "REOMET 39" (trade mark) ex Ciba Geigy).

The invention further comprises a process for the preparation of a fluid composition of the invention which comprises mixing at least one fluorohydrocarbon with at least one carboxylic acid ester of formula I as defined above.

The invention also comprises the use of a fluid composition of the invention as refrigeration fluid in compression refrigeration equipment, e.g. refrigerators and air-conditioners, including domestic and industrial air conditioning systems.

The carboxylic acid esters of formula I may readily be synthesised in known manner, e.g. by processes analogous to those described in WO 90/12849, or by processes according to or analogous to that described hereinafter in Example 1.

The invention will be further understood from the following illustrative Examples.

EXAMPLES 1 TO 12

Preparation of pentaerythritol tetrapentanoate (1)

To a mixture of pentaerythritol (227.9g, 2.0 mol) and pentanoic acid (887.2g, 8.6 mol) in a reactor fitted with a Dean and Stark trap was added, with stirring, under nitrogen, xylene (250ml) and methanesulphonic acid (40.8g, 0.4 mol). The resulting mixture was stirred under nitrogen for 5 hours at 140°C, before being cooled to ambient temperature (20°C), washed with 1M aqueous sodium hydroxide solution (2 x 500ml), washed with 10% w/v aqueous sodium sulphate solution (6 x 500 ml), dried (Na_2SO_4) filtered and evaporated under reduced pressure to yield pentaerythritol tetrapentanoate (1) (756g, 80%), characterised by viscosity at 40°C of 16.72 and at 100°C of 3.75 (DIN 51 562), viscosity index of 113 (DIN 150 2909) and saponification no. 484.7 (ASTM D1962-67).

Following analogous procedures, there were prepared a number of additional pentaerythritol esters (Examples 2 to 12). Details of these esters are given in Table 1 below, together with their viscosities at 40°C and 100°C (DIN 51 562), viscosity indices (VI) (DIN 150 2909), pour points (DIN ISO 3016) and saponification nos. (ASTM D 1962-67).

Miscibility of the various pentaerythritol esters with R134a refrigerant (1,1,1,2-tetrafluoromethane) was determined using a cryostat, a thermostat and glass tubes prepared according to DIN 51 351. Mixtures of refrigerant and pentaerythritol ester (concentrations determined gravimetrically) containing respectively 2% w and 20% w pentaerythritol ester were prepared in sealed glass tubes and the tubes were completely immersed in the temperature-controlled bath of the thermostat or cryostat. The bath fluid was then heated up or cooled down at a rate of 2°C/minute, and the temperature of phase separation was noted. Results are given in Table 1 following.

TABLE I

$C\ (CH_2.O.CO.R^1)_x\ (CH_2.O.CO.R^2)_y\ (CH_2.O.CO.R^3)_z$

$(x + y + z = 4)$

Example	R^1	x	R^2	y	R^3	z	Viscosity mm^2/s 40°C	Viscosity mm^2/s 100°C	V I	Pour Point °C	Sap. No.	Miscibility max/min °C 2%	Miscibility max/min °C 20%
1	$(CH_2)_3CH_3$	4	-	-	-	-	16.4	3.74	117	<-60	465	<-70/>100	<-70/>100
2	$(CH_2)_2CH_3$	4	-	-	-	-	16.0	3.47	87	-33	545	<-70/>100	<-70/>100
3	$CH_2CH(CH_3)_2$	4	-	-	-	-	42.1	5.58	51	-45	473	<-70/>100	<-70/>100
4	$(CH_2)_3CH_3$	3	$C(CH_3)(C_2H_5)_2$	1	-	-	23.0	4.43	101	-60	440	<-70/>100	<-70/>100
5	$(CH_2)_3CH_3$	3	$C(CH_3)_2CH_2CH_2CH_3$	1	-	-	22.2	4.32	102	<-60	435	<-70/>100	<-70/>100
6	$(CH_2)_3CH_3$	2	$C(CH_3)(C_2H_5)_2$	1	$C(CH_3)_2CH_2CH_2CH_3$	1	41.3	5.69	64	-48	398	<-70/>100	<-70/>100
7	$(CH_2)_3CH_3$	3	$C(CH_3)(C_2H_5)_2$	0.5	$C(CH_3)_2CH_2CH_2CH_3$	0.5	25.5	4.67	99	-60	450	<-70/>100	<-70/>100
8	$(CH_2)_3CH_3$	3	$C(CH_3)(C_2H_5)_2$	0.25	$C(CH_3)_2CH_2CH_2CH_3$	0.75	22.8	4.41	101	<-60	441	<-70/>100	<-70/>100
9	$(CH_2)_3CH_3$	2	$CH(C_2H_5)(CH_2)_3CH_3$	2	-	-	28.9	4.94	91	-60	386	<-70/>100	-58/>100
10	$(CH_2)_3CH_3$	1.33	$CH(C_2H_5)(CH_2)_3CH_3$	2.67	-	-	37.3	6.28	105	-57	347	-68/>100	-38/>100

TABLE I
(continued)

$C(CH_2.O.CO.R^1)_x(CH_2.O.CO.R^2)_y(CH_2.O.CO.R^3)_z$

(x + y + z = 4)

Example	R^1	x	R^2	y	R^3	z	Viscosity mm²/s 40°C	Viscosity mm²/s 100°C	V I	Pour Point °C	Sap. No.	Miscibility max/min °C 2%	Miscibility max/min °C 20%
11	$(CH_2)_3CH_3$	1	$CH(C_2H_5)(CH_2)_3CH_3$	3	-	-	35.6	5.6	91	-57	357.5	-68/>100	-40/>100
12	$(CH_2)_3CH_3$	1.6	$CH(C_2H_5)(CH_3)_3CH_3$	2.4	-	-	31.5	5.27	100	-57	376.1	-66/>100	-41/>100
Comp A	$CH(CH_3)_2$	4	-	-	-	-	----------SOLID----------						
Comp B	$(CH_2)_5CH_3$	4	-	-	-	-	21.7	4.74	142	-45		-20/>100	5/88
Comp C	$(CH_2)_6CH_3$	4	-	-	-	-	28.5	5.59	139	-9		-5/80	Immiscible
Comp D	$(CH_2)_7CH_3$	4	-	-	-	-	32.9	6.34	147	-12		40/72	Immiscible

It will be seen that the miscibiity data for the examples of the invention is significantly superior to that obtained for Comparative Examples A to D. This is particularly marked for Examples 1 to 8, in which all the groups R^1, R^2 and R^3 are C_{4-6} alkyl groups containing 3 or 4 chain atoms.

Claims

1. A fluid composition for use in compression refrigeration comprising a mixture of
   (a) at least one fluorohydrocarbon and
   (b) at least one carboxylic ester of a polyhydroxy compound, having the general formula

$$C(CH_2.O.CO.R)_n(R')_{4-n} \quad (I)$$

   wherein n is 3 or 4, R' represents a methyl or ethyl group and each R independently represents a C_{3-8} alkyl group containing 3 to 5 chain atoms.

2. A fluid composition according to Claim 1 wherein the fluorohydrocarbon is a tetrafluoroethane.

3. A fluid composition according to Claim 2 wherein the fluorohydrocarbon is 1,1,1,2-tetrafluoroethane.

4. A fluid composition according to any one of Claims 1 to 3 which comprises a mixture containing 70 to 99% w of the at least one fluorohydrocarbon and 1 to 30% w of the at least one carboxylic ester.

5. A fluid composition according to any one of Claims 1 to 4 wherein in formula I n is 4.

6. A fluid composition for use in compression refrigeration comprising a mixture of at least one fluorohydrocarbon and at least one carboxylic ester of a polyhydroxy compound, wherein the at least one carboxylic ester of a polyhydroxy compound consists of at least one ester having the general formula

$$C(CH_2.O.CO.R)_4 \quad (II)$$

   wherein n is 3 or 4, and each R independently represents a C_{3-8} alkyl group containing 3 to 5 chain atoms.

7. A fluid composition according to any one of Claims 1 to 6 wherein in formula I or II each R independently represents a C_{4-6} alkyl group containing 3 or 4 chain atoms.

8. A fluid composition according to any one of Claims 1 to 7 wherein the ester of formula I or II has viscosity at 40°C (DIN 51 562) of at least 20 mm^2/s wherein on average at least one R moiety is a branched alkyl group.

9. A process for the preparation of a fluid composition according to any one of Claims 1 to 8 which comprises mixing at least one fluorohydrocarbon with at least one carboxylic ester of formula I as defined in Claim 1.

10. Use of a fluid composition according to any one of Claims 1 to 8 as refrigeration fluid in compression refrigeration equipment.